

964845



PATENT SPECIFICATION

NO DRAWINGS

964845

Date of Application and filing Complete Specification: Sept. 10, 1962.
No. 34522/62.

Application made in Germany (No. D37006 IVd/39b) on Sept. 11, 1961.
Complete Specification Published: July 22, 1964.

© Crown Copyright 1964.

Index at acceptance:—C3 Q(C6A, C6B, C8B, C8C, D1A); C3 P(2C6A, 2C6B, 2C8B, 2C8C, 2D1A, 2K7, 2K8)

International Classification:—C 08 c (C 08 d)

COMPLETE SPECIFICATION

Light-Coloured and Light-Stable Plasticizer-Containing Rubber and Plastic Compositions

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, Holland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a light-coloured and light-stable plasticizer-containing rubber or plastic composition.

In processing natural and synthetic rubber and certain thermoplastics, e.g. polyvinyl chloride, plasticizers have to be added. Although the plasticizers may be incorporated in the solid polymerisates by mixing, it is also possible to add them during polymerization or to coagulate them as an emulsion with the corresponding latices.

Suitable plasticizers for the above purpose are in particular the high-molecular hydrocarbon mixtures predominantly consisting of aromatics, which mixtures have a strong tendency to form a gum with concentrated sulphuric acid and are obtained as extracts in refining mineral oils with selective solvents, e.g. phenol, furfural and liquid SO₂. It has also been proposed to use as a plasticizer or extender oil for rubber, mineral oils having a composition similar to that of the extracts. However, owing to their natural dark colour these products cannot be used for the production of light-coloured plastics or of oxidation-stable vulcanisates which have a light colour and do not darken when exposed to light. In particular, such plasticizers are not suitable when it is necessary to incorporate large quantities of plasticizer into compositions from which light-coloured plastics are to be obtained after vulcanization of the plasticizer-containing rubber compositions. Hence such plasticizer oils cannot be used

[Prior art]

for the manufacture of light-coloured rubber goods, and particularly light-coloured rubber sheets, in which large quantities of plasticizers are used. This is even the case when these plasticizers are subsequently refined with sulphuric acid and/or bleaching earth.

For this reason mineral oils of a predominantly naphthenic-paraffinic nature are used in the production of light-coloured rubber or plastic articles. This group of oils includes those either having good colour stability but a poor compatibility with rubber, or those having a relatively good compatibility with rubber but imparting a poor light resistance to the vulcanisates or plastic products. The first contain, for example, hardly any aromatic compounds whereas the oils of the second group normally have an aromatic compound content of more than 15%.

It has now been found that it is possible to manufacture light-coloured and light-stable plasticizer-containing rubber compositions and plastic products by using such plasticizer oils based on paraffinic-naphthenic mineral oils as are obtained by sulphuric acid and subsequent earth treatment of the raffinates obtained by extracting mineral oils with selective solvents and which have certain physical properties.

Accordingly the invention provides a light-coloured and light-stable plasticizer-containing rubber or plastic composition which contains as a plasticizer a naphthenic-paraffinic mineral oil obtained as raffinate by extraction of a mineral oil with a selective solvent, such as phenol, furfural and preferably liquid SO₂, and subsequent subjection to a sulphuric acid and earth treatment so as to obtain a naphthenic-paraffinic oil which is free from aromatic and other unstable components to such an extent that it has a viscosity gravity constant of less than 0.85, a pour point of less than -30°C, a solubility in 96% sul-

45

50

55

60

65

70

75

80

85

phuric acid of at least 40% and a maximum Union colour of 1½.

Various methods are used in the petroleum industry to characterize crude oil. The viscosity gravity constant gives a numerical value to the terms "paraffinic" and "naphthenic". The value of the viscosity density constant is based on the fact that Pennsylvanian crude (USA), a paraffinic oil, has a lower density than a naphthenic oil of the same viscosity. The scale for this constant varies from approximately 0.800 for a typical paraffinic oil up to 0.900 for a typical naphthenic oil.

The amount of carbon contained in the naphthenic mineral oil which is used as plasticizer in the composition according to the invention varies from 0%—15%, preferably from 5%—10%, in the aromatic function from 35%—50%, preferably from 38%—45%, in the naphthenic function and from 45%—60%, preferably from 50%—55%, in the paraffinic function, the percentages being based on the total weight of carbon present.

The composition may additionally contain suitable fillers, e.g. carbon black and silica clay.

The Union colour is determined by means of the Union Colorimeter according to ASTM D155—45T. In this apparatus the oil samples are successively compared in a standard glass jar with 12 glass colour standards, illuminated by a light source. The Union colour numbers run from 1 (light)—8 (dark).

The advantage of the plasticizers according to the invention is that they no longer contain any constituents which tend to darken upon ageing. They nevertheless possess good compatibility with rubber and plastics and impart good physical and chemical properties to the final products, in particular an outstanding light resistance. This is also the case

when the relevant plasticizers are used in amounts of more than 40%, for example with rubber. "Rubber" as used herein is intended to include natural rubber as well as synthetic rubber, for example the polymerisates or copolymerisates of butadiene, its homologues (for instance methyl butadiene or isoprene), its derivatives, including co-polymerisates of butadiene with styrene or acrylonitrile and butyl rubber. By the term "plastic" is meant any type of addition or condensation polymer, for example phenolic, polyvinyl or acrylic polymers, and polyolefins such as polyethylene, polypropylene and copolymers of ethylene and propylene.

It is possible to incorporate or coagulate the present plasticizers in the rubber or plastic by the usual methods or together with suitable fillers. Thus, a plasticizer emulsion may be blended in the synthetic rubber emulsion or emulsified in the aqueous rubber emulsion after which the emulsion mixture is coagulated. The resultant coagulums are then processed in the usual way. However, the mixture of rubber or plastic with the mineral oils of the invention may also be processed in known mixing and kneading equipment.

The favourable properties of the plasticizers of the invention are shown by the following test results obtained with rubber vulcanisates containing 37.5% of an oil according to the invention and for comparison rubber vulcanisates containing two clear commercial plasticizers. The vulcanisates containing oils according to the invention have outstanding oxidation stability and consequently light resistance after weathering or treatment with ultra-violet light.

Discoloration of the vulcanisates

(Reflection values in the Hunter reflectometer: green filter, small shutter, neutral filter 0.5)

Oil	unilluminated	75 hrs UV-Lamp	9 days weathering
Plasticizer (of invention)	85	70	81
Plasticizer I (commercial)	85	60	75
Plasticizer II (commercial)	82	49	58

The remarkable feature of the plasticizers of the invention is that they not only impart very good light resistance to the vulcanisates but also possess a better plasticiz-

ing effect, as can be seen from the Mooney viscosities of an unvulcanized tyre tread stock

	Plasticizer (of invention)	Commercial light-coloured plasticizer	
		I	II
Mooney viscosity	42	50	52

From the compositions provided by the invention, articles, such as tyres, shoesoles, bathmats, gloves and toys may be manufactured in a manner known per se. Where necessary, the compositions may first be admixed with curing agents, fillers, and/or lubricants.

WHAT WE CLAIM IS:—

1. Light-coloured and light-stable plasticizer-containing rubber or plastic composition which contains as a plasticizer a naphthenic-paraffinic mineral oil obtained as raffinate by extraction of a mineral oil with a selective solvent and subsequent subjection to a sulphuric acid and earth treatment so as to obtain a naphthenic-paraffinic oil which is free from aromatic and other unstable compounds, to such an extent that it has a viscosity gravity constant of less than 0.85, a pour point of less than -30°C , a solubility in 96% sulphuric acid of at least 40% and a maximum Union colour of $1\frac{1}{2}$.
2. A composition according to claim 1 in which the selective solvent for the mineral oil is phenol or furfural.
3. A composition as claimed in claim 1 in which the selective solvent for the mineral oil is liquid SO_2 .
4. A composition according to any preceding claim containing as a plasticizer a mineral oil which contains such quantities of aromatic, naphthenic and paraffinic compounds that the

amount of carbon contained in the aromatic function ranges from 0% to 15%, in the naphthenic function from 35% to 50%, and in the paraffinic function from 45% to 60%, the percentages being by weight of the total carbon present.

5. A composition according to claim 4 containing as a plasticizer a mineral oil which contains such quantities of aromatic, naphthenic and paraffinic compounds that the amount of carbon contained in the aromatic function ranges from 5% to 10%, in the naphthenic function from 38% to 45% and in the paraffinic function from 50% to 55%, the percentages being by weight of the total carbon present.

6. A composition according to any preceding claim, additionally containing a filler.

7. A composition according to claim 6 in which the filler is carbon black, silica, clay or a mixture containing any of these.

8. Composition according to claim 1 substantially as hereinbefore specifically described.

9. Articles whenever made from a composition according to any preceding claim.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24 Southampton Buildings, Chancery Lane,
London, W.C.2.